# THE ELECTRONIC AND PHOTOCHEMICAL DECOMPOSITIONS OE POTASSIUM CHLORATE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1929

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# THE ELECTRONIC AND PHOTOCHEMICAL DECOMPOSITIONS OF POTASSIUM CHLORATE

The chemical effects of alpha and beta particles have been studied in some detail during the past few years.[1] These studies have served to demonstrate an equivalence between the extent of ionization and the amount of chemical reaction produced. It has also been shown[2] that reactions initiated by electron bombardment obey laws very similar to those applicable to $\alpha$-particles. Other reactions have been studied in an effort to determine the minimum kinetic energy of electron which will produce an effect. Thus ammonia is formed in a mixture of nitrogen and hydrogen when these gases are under the influence of electrons of speed greater than those corresponding to the ionization potentials of both reacting gases.[3]

The present work was undertaken with the object of ascertaining whether solid potassium chlorate could be decomposed by slow speed electrons and to ascertain whether any relationship could be found between the kinetic energy of the electrons and the wave length of radiation necessary to bring about photochemical decomposition. The conditions for photochemical decomposition have been obtained, but the results on the electronic decomposition are somewhat less conclusive. They indicate, however, that solid potassium chlorate may be decomposed by fairly high speed electrons.

## I. Experimental Procedure

(a) **The Electronic Decomposition.**—Preliminary studies[4] indicated that solid oxalic acid could be decomposed by electron bombardment

[1] For review, see Lind, "The Chemical Effects of Alpha Particles and Electrons," 2d ed., The Chemical Catalog Co., Inc., New York, **1928.**

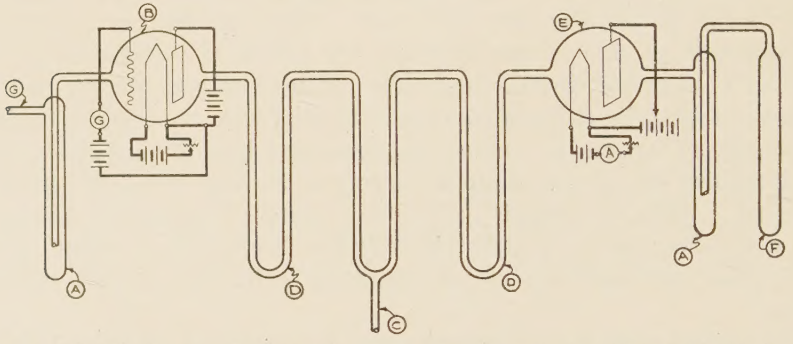
[2] See, for example, Marshall, *J. Am. Chem. Soc.*, **50,** 3178 (1928); Busse and Daniels, *ibid.*, **50,** 3271 (1928); Kruger and Moeller, *Physik. Z.*, **13,** 1040 (1912); Kruger and Utesch, *Ann. Physik*, **78,** 113 (1925).

[3] Hiedeman, *Chem.-Ztg.*, **45,** 1073 (1921); **46,** 97 (1922); Anderson, *Z. Physik*, **10,** 54 (1922); Storch and Olson, *J. Am. Chem. Soc.*, **45,** 1605 (1923).

[4] For mention, see Noyes and Vaughan, *Chem. Reviews* (to appear in the near future).

when the kinetic energy of the electrons exceeded a value corresponding to between 4.5 and 5.5 volts. In this study a filament was used as a source of electrons and their speeds were limited by grids in the ordinary way. The results obtained were open to question for the following reasons: (1) the charge on the solid may have rendered the velocity of the electrons uncertain; (2) oxalic acid does not have a negligible vapor pressure at room temperature;[5] (3) thermal radiation from the filament may have caused a slight amount of decomposition. This error was probably small.

To meet these objections partially it was decided to undertake a similar study of solid potassium chlorate, since it has a negligible vapor pressure at ordinary temperatures. Moreover, it undergoes a decidedly exothermic decomposition, which should cause any decomposition initiated by an electron to be magnified by an expected chain reaction.




A, Liquid-air trap; B, ionization gage; C, mercury shut-off; D, liquid-air trap; E, reaction vessel immersed in liquid air; F, mercury reservoir; G, to McLeod gage and pumps.

Fig. 1.—Schematic diagram of apparatus.

The method used in the electronic decomposition of solid potassium chlorate is similar to that used in work on critical potentials. It was necessary to simplify the apparatus by omitting the grids in order to increase the electron current.

Figure 1 shows a schematic diagram of the apparatus used. It was attached to the usual high vacuum line. The vacuum attainable was limited only by the vapor pressure of mercury at liquid-air temperatures (below $10^{-9}$ cm.).[6] The ionization gage (B) was the Poindexter modification[6] of the Buckley type,[7] depending on the ionization of the gas by electrons. The volume was only 250 cc., due to the necessity of developing an apparatus which could be thoroughly outgassed by baking in a furnace. The ionization gage was capable of measuring changes in pressure of $10^{-8}$ cm.

The reaction vessel was a two-electrode vacuum tube (E). The source of electrons was a hot filament in the shape of a spiral one centimeter in length containing three

[5] Noyes and Wobbe, *J. Am. Chem. Soc.*, **48**, 1882 (1926).

[6] Poindexter, *Phys. Rev.*, **26**, 849 (1925).

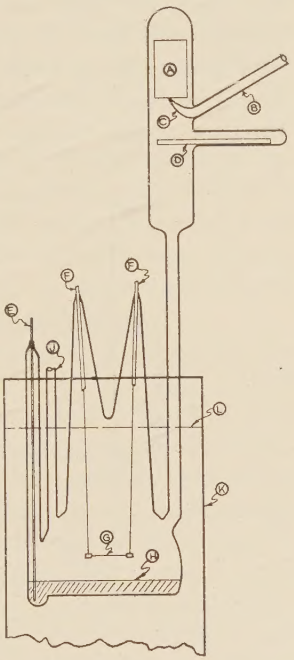
[7] Buckley, *Proc. Nat. Acad. Sci.*, **2**, 683 (1916).

centimeters of tungsten wire. The first tubes had a metallic plate. It was found, however, that the potassium chlorate decomposed slightly before it was subjected to bombardment with electrons. Figure 2 shows the type of reaction vessel used in the final experiments. It was designed to meet the following requirements: (1) to fit in a quart Dewar vessel; (2) to facilitate the conduction of heat away from the potassium chlorate; (3) to have the major portion immersed in liquid air with only the seals above the liquid air level. In order to meet the second of these requirements a mercury plate was substituted for the solid metallic plate.

The entire apparatus, including the ionization gage, was first outgassed in a furnace heated to about 500° for eight hours. The part of the line not included in the furnace was kept hot by a hand torch. The liquid-air traps were then surrounded by liquid air and the filaments lighted. The plate and grid of the ionization gage were outgassed by bombardment with electrons accelerated through a potential of 10,000 volts. This treatment lasted for three hours. This prolonged outgassing not only removed adsorbed gases and vapor, but also the tungsten oxide coating sometimes formed on the inside of the ionization gage during the early stages of the outgassing.

After the outgassing the reaction vessel was cooled in a salt–ice bath and the mercury distilled into it. The reaction vessel was then immersed in liquid air and the solid mercury plate subjected to electron bombardment. No change in pressure was recorded by the ionization gage after a long interval. The entire process was repeated until no change in pressure was observed on standing for a twenty-four hour period.

The potassium chlorate (which had been kept in a vacuum desiccator over phosphorus pentoxide for six months) was now introduced into Tube B (Fig. 2) and sealed off. The weight A was raised by an electromagnet and allowed to drop. The weight was prevented from falling into the reaction vessel by the catch D. In this manner the potassium chlorate and a small amount of air were admitted to the reaction vessel while the vacuum pumps were running. The line was evacuated with the liquid air removed from around the reaction vessel and allowed to stand for twelve hours. A final evacuation was made before an experiment was started.



A, Soft iron plunger; B, side tube for potassium chlorate; C, drawn out tip to be broken by plunger; D, brass rod which stops the plunger; E, to accelerating voltage; F, filament leads; G, filament; H, mercury plate; J, mercury filler; K, Dewar flask with liquid air; L, liquid-air level.

Fig. 2.—Diagram of reaction vessel.

The mercury, H, was then given a negative potential with respect to the filament G and the filament lighted until an equilibrium condition was obtained, *i. e.*, until there was no further diffusion of traces of air from the ionization gage to the reaction vessel or *vice versa*. During this time the reaction vessel was surrounded by liquid air. The mercury was now raised in the cut-off, C (Fig. 1), and the electrons were accelerated toward the potassium chlorate in the reaction vessel with a definite voltage. The two traps, D, were, of course, immersed in liquid air. The liquid air was continually replenished around the reaction vessel and the traps to keep conditions as nearly constant as possible.

Due to the gradual change of the storage batteries and to vibration in the building, there was a continual drift in the current through the ionization gage which could not be ascribed to a change in pressure. Accordingly, after one and three-fourth hours, the positive-ion current through the ionization gage was determined at two-minute intervals for fifteen minutes and then the mercury in the cut-off, C, was lowered and readings again taken at two-minute intervals. Any gas admitted to the ionization gage from the reaction vessel at this time would cause a change in the slope of the current–time curve. By this method a change in pressure of $10^{-8}$ cm. should be detectable.

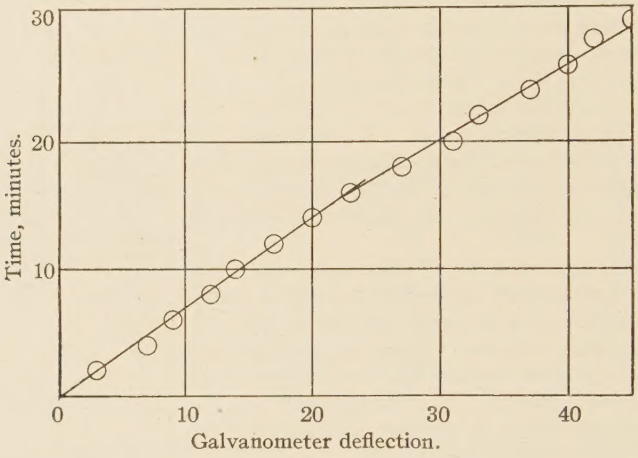



Fig. 3.

Figure 3 shows one typical curve when the accelerating voltage in the reaction vessel was 22 volts. There is a change in slope in the middle of the curve which indicates quite definitely that there was a real decomposition of the potassium chlorate brought about at this voltage. Curves at lower potentials showed no breaks which could be ascribed definitely to an increase in pressure. The experimental error in the determination of the minimum voltage is quite large.

There are two complicating factors which might make the detection of any reaction by this method difficult. The first of these is the adsorption of oxygen by the walls of the apparatus at liquid-air temperatures. This problem has been investigated by Langmuir.[8] He developed the equation $Q = abp/(1 + ap)$, where $Q$ is the quantity of gas adsorbed in mm.$^3$ (measured at standard conditions) per cm.$^2$ of surface, $a$ is a constant, 0.079, $b$ is a constant, 8.46 and $p$ is the pressure in dynes per cm.$^2$ This equation is not valid at very low pressures, but may be used to determine the order of magnitude of the adsorption. It can be shown that

[8] Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).

if the surface at liquid-air temperatures is 200 cm.$^2$, the volume 1 liter and the bombarding current $10^{-8}$ amp., the decomposition should be detectable on the ionization gage without any difficulty if one electron causes the formation of one gas molecule. The second factor is the chemical clean-up. This matter has been discussed by Dushman.[9] Since the maximum pressure to be expected if one molecule of oxygen is liberated per electron passing through the reaction vessel is $10^{-5}$ cm., the chemical clean-up would undoubtedly reduce the pressure just about to the limit detectable by the ionization gage.

In view of these considerations it seems probable that detection of the decomposition would be difficult and would not be decisive unless a short chain reaction (say 10 to 100 molecules in length) were initiated by the electron bombardment. The only curves which showed any definite break were at accelerating potentials of 22 volts. This may possibly be ascribable to the slightly greater current at this potential.

(b) **The Photochemical Decomposition.**—Preliminary work on the photochemical decomposition of solid potassium chlorate was carried out with various glasses as color filters. It was found at first that there was an apparent photochemical decomposition brought about by radiation transmitted by soft glass unless the potassium chlorate was separated from the evacuating pumps and McLeod gage by a trap immersed in carbon dioxide snow and ether. Whether this means that there is some secondary reaction between potassium chlorate and mercury vapor was not investigated. When mercury vapor was removed, it was found that no decomposition could be produced by radiation from either a carbon or an iron arc except through quartz itself. All of the color filters excluded the active radiation. The solid was prevented from warming up by immersion of the reaction vessel in water. The pressure changes were measured by a quartz fiber manometer.[10]

The final measurements were made with a constricted arc[11] and a monochromatic illuminator with quartz prisms and lenses. The potassium chlorate was dried at a temperature of 105° for several days under a high vacuum and during illumination mercury vapor was excluded by a trap immersed in liquid air. The liquid air was removed from the trap in making the pressure reading.

With the monochromatic illuminator set at 313m$\mu$ no decomposition was observed, whereas decomposition was observed with the setting at 253m$\mu$. The purity of the radiation was tested by photographing the spectrum with a quartz spectrograph. With the setting at 313m$\mu$, lines down to 280m$\mu$ were faintly visible and with the setting at 253m$\mu$ lines

[9] Dushman, *Gen. Elec. Rev.*, **24**, 440 (1921).

[10] Haber and Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).

[11] Forbes and Harrison, *J. Am. Chem. Soc.*, **47**, 2449 (1925).

up to 290m$\mu$ were detectable. No setting of the illuminator which completely excluded the 253.7m$\mu$ line of mercury caused any observable decomposition.

As a result of these experiments, it would seem that photochemical decomposition of potassium chlorate to give oxygen may be brought about by radiation of wave length below 280m$\mu$. It would not seem possible to make any more accurate determination of the photochemical threshhold than this. The line at 313m$\mu$ is much more intense than the line at 253.7m$\mu$. The lines in between are relatively weak in intensity.[11]

The quantum efficiency is of the order of 1/100 at 253.7m$\mu$, neglecting radiation scattered by the solid.

## II. Discussion of Results and Conclusions

The wave length required to produce photochemical decomposition of solid potassium chlorate is found to correspond to about 4.5 to 5.0 volts. The experiments on the electronic decomposition indicate that electrons of this kinetic energy do not cause a rapid decomposition of the potassium chlorate. The fact that from 10 to 100 molecules would have to decompose per electron to be conclusive would make any definite decision on this point impossible. There is the further difficulty in dealing with an insulating solid that the surface might well acquire a charge which would reduce the kinetic energy of the electrons below the threshold value. However, any decomposition at 20 volts would lead to the production of ionization in the gas phase, a fact which would lead to a partial dissipation of the surface charge as well as superimposing a photochemical on the electronic decomposition. It would seem entirely probable, therefore, that even with a decomposition of one molecule per electron at this high voltage, the resulting amplification would have made the effect detectable.

The possibility of increasing the rotation of a diatomic molecule to such a point that dissociation results is negligible, for the selection principle makes changes in rotational quantum number by $\pm 1$ only possible. Molecules may be dissociated, however, by increasing the vibrational quantum number beyond the convergence limit. For certain types of molecule this may be accomplished directly by the absorption of radiation. Dissociation may be produced by increasing the vibrational quantum number to such a point that change in electron level becomes possible. Dissociation of the excited molecule results if it possesses the requisite amount of energy. Thus hydrogen should be dissociated by energy corresponding to 4.46 volts[12] but radiation of this wave length is not absorbed by $H_2$ molecules and inelastic collisions of electrons in hydrogen are not observed at this voltage. However, it is possible to dissociate hydrogen

[12] Richardson and Davidson, *Proc. Roy. Soc. London*, **123A**, 466 (1929).

by wave lengths below 90m$\mu$ with the production of one normal atom and one atom in a two quantum state.

If a molecule is to be dissociated by electron impact, it may happen that an energy greater than that theoretically necessary for dissociation would be required. That is, to change the electron level without change in vibrational quantum number it may be necessary to add energy greater that that necessary to bring the molecule in the new electron state to dissociation. Hence the voltage required for dissociation may not agree with that calculated from spectroscopy, for there seem to be few if any cases on record where vibrational quantum number is changed by electron impact without accompanying change in electron level. In most cases the difference is not very great. For these reasons we see that it may not necessarily be possible to calculate the wave length required for photochemical decomposition from the kinetic energy of the electron which will produce the change and *vice versa*. Thus the simple relationship $eV = hc/\lambda$ ($e$ is the charge on the electron, $V$ is the accelerating voltage, $h$ is Planck's constant, $c$ is the speed of light and $\lambda$ is the wave length) may not hold for the types of process referred to. In so far as conclusions are justified from these experiments, it would seem that there is lack of agreement between the two phenomena for solid potassium chlorate and that the activating processes are probably different.

The phenomenon of pre-dissociation[13] may be of importance in the photochemical decomposition of solids. That is, when the electron level is changed, the molecule may be in such a vibration state that change to another electron level becomes possible with resultant dissociation. For complicated molecules this type of process may easily occur. A diffuseness of the absorption bands is an indication of this phenomenon. Little quantitative work on the absorption spectra of solids has been done which would permit conclusions to be drawn on this point, although it is true that sharp absorption lines are not usually observed.

## Summary

1. An attempt has been made to study the decomposition of solid potassium chlorate by bombardment with slow electrons. The results indicate that decomposition may be brought about by 22-volt electrons. Results with lower voltages are somewhat inconclusive but are, on the whole, negative.

2. Oxygen is evolved from solid potassium chlorate by the action of radiation of wave length shorter than about 280m$\mu$.

3. A brief theoretical discussion is given.

[13] Henri and Teves, *Nature*, **114**, 894 (1924).